Roll to Roll Printing of Aqueous Pristine Graphene Dispersions

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Since the isolation and observation of graphene[1] there have been a vast number of proposed applications for the material. With applications ranging from photovoltaic devices[2], touchscreens[3], energy storage[4] and transistor electronics[5] the potential for graphene appears almost limitless. However the commercial realisation of each application depends on graphene being produced and deposited in a cheap, accurate and rapid manufacturing environment. This work aims to develop a stable water based graphene solution and then deposit the graphene using a number of printing methods.

Graphene production techniques can be classified into two types; top down and bottom up. Bottom up production describes the growth of graphene using epitaxial or CVD growth techniques. This tends to result in high quality films and growth can be patterned precisely. However growth techniques tend to require high temperatures and catalyst materials, limiting the choice of substrates. Bottom up growth methods tend to require environments and timescales that are unsuitable for roll to roll production techniques, though batch roll lamination of large area CVD grown graphene sheets has been demonstrated.

Top down production techniques tend to separate the graphene sheets from a graphite precursor. This can be performed in many ways, the most famous being the mechanical exfoliation method[1]. Other separation methods include sonication in suitable solvents[6], reduction of graphene oxide and non covalent functionalization of graphene in solution by stabilizers. Unlike bottom up methods, top-down production methods allow for direct preparation of graphene dispersions or mass production of graphene powders, which can then be dispersed in suitable solvents and deposited on proper substrate for further device manufacturing. This will result in lower production costs and timescales, but at the same time the conductivity and optical performance of graphene films may be hindered due to an increased contact resistance between multilayers of graphene. However this method will still be suitable for many applications, such as catalyst layers in dye sensitized photovoltaic cells which require large available surface areas for which graphene powder will be preferable to large area flakes.

The initial stage of this research focused on the production of stable graphene solutions while avoiding the use of conventional stabilizers such as surfactants. In first step, an aqueous solution of expanded graphite and functionalized pyrene derivatives (or "π-π stackers") was sonicated to increase the interlayer spacing of graphene sheets. These stacker molecules adsorb on the surface of graphene layers through π-π interactions between their aromatic basal planes. They prevent reaggregation of graphene sheets by inducing steric and electrostatic repulsion forces between separated sheets[7,8]. The process was followed by centrifugation step to remove undispersed graphite from the final graphene solution. Compared to conventional stabilizers such as surfactants, these pyrene derivatives yield higher concentrations of graphene per mass of stabilizer.

These solutions were then tested with a variety of solution deposition methods to assess their suitability for further device production. Initial tests focused on inkjet printing, a method that is ideal for low viscosity solutions but limiting with respect to flake size due to the jetting nozzle diameter. The solution was characterised to identify suitability for inkjet printing and it was found that the viscosity was below recommended specifications and the surface tension was too high, however the solution was jettable. An image of an inkjet print onto a Si wafer is shown in figure 1. Strategies for further optimisation of the fluid for inkjet printing have been identified and further research is ongoing.

The solution was also deposited using a flexographic printing technique. This technique allows for higher speeds than inkjet printing at the expense of feature resolution. Traditionally flexographic inks need to have higher viscosities than inkjet inks, however techniques have been developed to partially overcome these limitations and enable the flexographic printing of homogenous features using low viscosity inks. This will allow minimisation of additive usage in the ink, which will tend to have a detrimental effect on the electronic properties. Applying these techniques allowed features to be successfully printed. Analysis of the electronic performance of these prints is also ongoing.

In conclusion, stable water based graphene dispersion has been produced using pyrene derivatives instead of surfactants. This dispersion has then been deposited using two contrasting printing methods. This work demonstrates the dispersion suitability for use in high speed, roll to roll device manufacture, which is one of the keys to unlocking the commercial promise of graphene.

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Figures

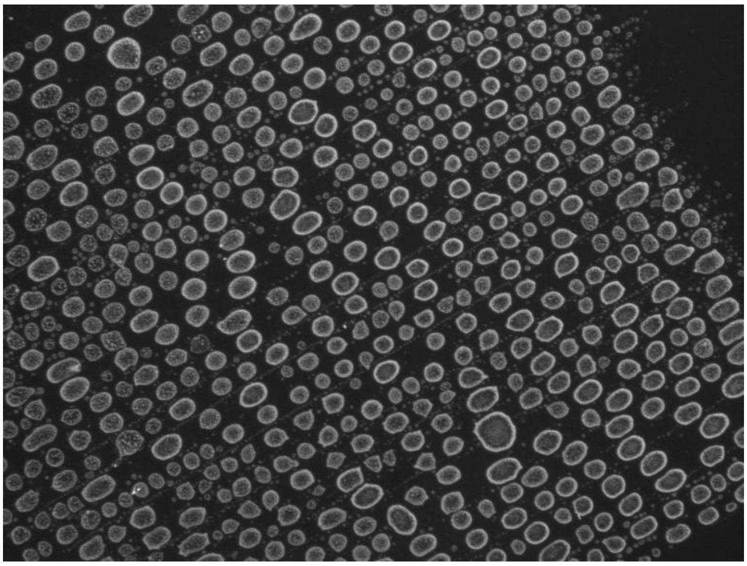

Figure 1. 6.5x optical image of aqueous graphene solution inkjet printed onto Si wafer.